Effect of watering and soil moisture on mercury emissions from soils

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Abstract. This paper presents data from experiments that measured Mercury (Hg) flux as a function of water addition and subsequent soil drying, and maintenance of soil water content over time utilizing small dynamic gas exchange chambers and large mesocosms. When soil surfaces were dry and water was added at an amount less than that necessary to saturate the soil an immediate large (relative to dry soil flux) release of Hg occurred. Diel Hg emissions from soils, unenriched ($0.02~\mu g~g^{-1}$) and enriched ($3~\mu g~g^{-1}$) in Hg and wet below saturation, were significantly elevated above that occurring from dry soils (2–5 times depending on soil water content) for weeks to months. Enhancement of emissions from wet soils in direct sunlight were greater than that from soils shaded or in the dark suggesting that a synergism exists between soil moisture and light. When soils were watered to saturation Hg emissions were suppressed or remained the same depending on the degree of saturation. It is hypothesized that the addition of soil water in amounts less than that necessary to saturate the soil surface results in an immediate release of elemental Hg from soil surface as the more polar water molecule out competes Hg for binding sites. As the water moves into the soil, Hg adsorbed to soil particles is desorbed into soil gas and dissolved in the soil water. The process of evaporation facilitates movement of Hg as mass flow to the soil surface where it is made available for subsequent release. The latter is hypothesized to be an important process by which Hg is recharged at the soil–air interface.

Introduction

In order to estimate mercury (Hg) emissions from soils, those processes controlling emissions and their relative forcing potential must be understood. It has been demonstrated that temperature (Lindberg et al. 1979; Gustin et al. 1997), light (Zhang et al. 2001; Gustin et al. 2002), air Hg concentration (Engle et al. 2001), air chemistry (Engle et al. 2004), and soil Hg concentration (Rasmussen et al. 1998; Zehner and Gustin 2002) are important parameters controlling emissions. Algorithms have been developed using some of these parameters, allowing us to estimate Hg flux from substrates (cf. Engle et al. 2001; Coolbaugh et al. 2002; Engle and Gustin 2002; Zehner and Gustin 2002). Several studies have demonstrated that with the addition of water, Hg is immediately released from dry soil (Lindberg et al. 1999; Frescholtz and Gustin 2004; Nacht and Gustin 2004). These studies showed that small additions of water (not enough to

saturate the soil) significantly enhanced Hg emissions from dry desert soils. Frescholtz and Gustin (2004) demonstrated for one soil type, as the Hg concentration of the substrate was increased, the amount of Hg released with the addition of water increased. Lindberg et al. (1999) proposed three mechanisms that could be associated with the enhanced release of Hg observed with a precipitation event on dry desert soil: (1) physical displacement of elemental Hg (Hg^o) enriched soil gas by water filling the soil pores; (2) replacement of Hg^o adsorbed to the soil by H_2O molecules; and (3) desorption of Hg(II) bound to the soil and subsequent reduction to Hg^o. Frescholtz and Gustin (2004) found no simultaneous increase in CO_2 flux with watering in controlled laboratory experiments and suggested that this indicated that microbial activity in the soil was not responsible for the increased flux with watering.

This study focused on investigating the effect of irrigation and soil water content on Hg flux from unenriched and Hg-enriched soils through controlled experiments using small dynamic flux chambers and large mesocosms. With the large mesocosms, the influence of the presence of vegetation on the watering effect was also investigated. The objective was to derive a conceptual model to explain the mechanism responsible for enhanced Hg release from substrates due to water addition and to investigate the effect of long-term maintenance of elevated soil water content on Hg emissions.

Methods

Dynamic gas exchange chamber

Polycarbonate dynamic gas exchange or flux chambers (cf. Engle et al. 2001) of 1 l volume were used to measure Hg flux from ~5 l of soil contained in tubs (39×28×16 cm) located in a temperature-controlled greenhouse. Prior to any experiments, soils equilibrated in the tubs for at least 30 days. Two soil types were used in the tub experiment, one that was naturally Hg-enriched (3 ± 1 μg g^{-1}) and derived from weakly argillically altered andesite collected near Reno, Nevada, USA, and an unenriched soil with low Hg concentrations (0.015 ± 0.005 μg g^{-1}) collected from the same field site in Oklahoma as the tall grass prairie monoliths described below. Two tubs of the latter were amended with $HgCl_2$ to enrich the soil Hg content to 0.1 ± 0.05 μg g^{-1}. Mercury enriched and unenriched soils had different physical properties, including bulk density (1.28 and 1.4 g cm^{-3}, respectively), capillary pore space (44 and 32%), and water holding capacity (34 and 23%) (A and L Great Lakes Laboratories, Inc.). The enriched Nevada soil was ~44% sand, 30% silt, and 26% clay with 3.1% organic matter, whereas the unenriched Oklahoma soil was ~50% sand, 29% silt, and 21% clay with 2.0% organic matter (A and L Great Lakes Laboratories, Inc.). The Hg flux response to wetting to 23% soil water content (SWC) and subsequent drying, and to maintenance of 13% SWC for ~50 days and 23% for ~14 days were measured for both soils. For all tub experiments

clean water (Millipore$^®$ filtered; 0.1 ± 0.1 ng Hg L^{-1}) was added using a light misting spray bottle. SWC was determined gravimetrically. To maintain SWC for the long-term experiments, water was added late in the afternoon each day. During all these experiments, air temperature, incident radiation (Li-Cor 190SA quantum sensor), and soil temperature (Omega soil thermocouples) adjacent to and under the flux chamber were monitored. Data were averaged over 5 min intervals and stored using a Campbell$^®$ Scientific data logger.

Mercury fluxes directly associated with the soil surfaces in the mesocosm experiments (described below) were measured using dynamic flux chambers. For the experiment using Hg contaminated soils, the chamber applied was clear cylindrical polycarbonate and had a 2 l volume. Similar to the chamber described above, 16 holes were located equidistant around the circumference to allow for unrestricted flow. For the tall grass prairie mesocosm experiments, the polycarbonate chamber was 1.4 l in volume and was placed on permanent PVC rings in the monoliths. These rings were used to keep small areas of bare soil available for gas flux measurements and extended about 2 cm into the soil. This chamber had 10 holes of 1 cm diameter equally distributed along the perimeter. The turnover rates for the chambers used on Hg enriched soils were 0.3 times a minute, whereas for the chambers on soils with low Hg concentrations, a turnover of 0.9 times per minute was used. The lower turnover for the latter allowed us to observe diel trends in fluxes, which were not observed at higher flow rates.

For all flux chamber experiments, air Hg concentrations were measured using a Tekran$^®$ (Tekran Inc., Toronto, Canada) 2537A Hg analyzer and Tekran$^®$ Automated Dual Switching Unit. Inlet and outlet air concentrations were measured in 5 or 10-min intervals resulting in a flux calculation every 10–20 min. Flux was calculated using the following equation:

$$F = C_o - C_i / Q * A,$$

where F equals flux in ng m^{-2} h^{-1}, C_o is concentration of Hg in air at the outlet and C_i is concentration at the inlet in units of ng m^{-3}, Q is the flow of air through the chamber in m^3, and A is the surface area exposed in the chamber in m^2. For the chamber flux measurements, inlet air Hg concentrations were measured at 2 cm height adjacent to the holes on the side of the chamber, and the outlet air concentration was measured in air being evacuated at the top and center of the chamber.

Mesocosm experiments

Two experiments used the Ecologically Controlled Enclosed Lysimeter Laboratories (EcoCELLs) at Desert Research Institute, Reno, NV. These very large totally enclosed mesocosms ($7.3 \times 5.5 \times 4.5$ m ($l \times w \times d$)) are naturally lighted plant growth and gas exchange chambers (Griffin et al. 1996; Gustin et al. 2004; Obrist et al. 2004). Within each EcoCELL are three lysimeter/rhizotron

weighing containers or pots (2.85×1.35×1.8 m). One experiment utilized two EcoCELLs with each pot filled with a base of ∼5 tons of gravel overlain by a liner and ∼4.5 tons of sandy loam topsoil amended with Hg containing mill tailings, resulting in a substrate Hg concentration of 12.3 ± 1.4 $\mu g\ g^{-1}$ (cf. Gustin et al. 2004). The form of Hg in the mill tailings was primarily Hg bound to Ag–Au–Fe sulfides, with $<0.05\%$ as volatile and $<0.2\%$ as readily leached forms (Sladek et al. 2002). In this experiment, temperatures were maintained at 18 °C during the night and 26 °C during the day; however, diel and seasonal changes in soil temperature were observed due to fluctuations in solar radiation (Gustin et al. 2004). Water was added directly to the pot surface by a drip irrigation system. Percent moisture was monitored weekly in each pot with Time Domain Reflectometry (TDR) probes (model 6005L2) and a Tektronix 1502C cable tester. In addition, the amount of water added and lost from each pot was continuously measured using balances at the corner of each pot (Griffin et al. 1996). Pots were watered to maintain SWC at 15–20% for the top 5–20 cm and 20–30% for the lower depths (30–50 cm), and no water drained from the pots. As the plants were growing, watering was adjusted based on plant needs. During the first year, approximately 100 one-year-old bare-rooted dormant whips (15 ± 5 cm height) of *Populus tremuloides* (quaking aspen) were planted in each of the two EcoCELLs, and in the second year only one of the two EcoCELLs used was planted.

For the second mesocosm experimental design, 12 large monoliths ($2.4 \times 1.2 \times 1.7$ m^3, $l \times w \times d$) of tall grass prairie soil and vegetation, obtained from Norman, Oklahoma, USA, were used (Obrist et al. 2004). Great care was taken to ensure that the monoliths remained intact and were undisturbed during excavation and transport to Reno, Nevada, USA. Three monoliths were placed in each EcoCELL. Watering for this project was done irregularly in amounts and frequency similar to precipitation patterns in Oklahoma using a ceiling mounted rain simulator. Water additions and amounts were measured using the same methods as described for the previous experiment. Temperatures were controlled over the experiment to mimic diel and seasonal trends measured in Oklahoma. Total Hg concentrations in monolith soils measured near the top of the soil profile (0.020 ± 0.001 $\mu g\ g^{-1}$ at 1 cm depth) were greater than those measured in deeper soils (e.g., 0.004 ± 0.0002 $\mu g\ g^{-1}$).

For both experiments, Hg concentrations in air were measured with a Tekran® 2537A Hg analyzer and a solenoid switching unit. The Tekran was autocalibrated nightly and a Tekran standard addition unit was used to permeate a known amount of Hg into the air stream being sampled at least 4 times a day. The latter provided a means of monitoring the recovery efficiency of the cartridges collecting Hg. Mercury flux for each EcoCELL was calculated based on the concentration of Hg in the incoming air and in the center of each EcoCELL, the surface area of the soil, and the flow rate of air into the mesocosm. The Hg concentration difference between incoming air and that in the empty EcoCELLs, after the Hg-contaminated soil experiment and prior to the placement of the tall

grass prairie monoliths in the EcoCELLs, was 0.03 ± 0.05 ng m^{-3} ($n = 700$) and not statistically significantly different from zero (t-test, $p < 0.05$).

In both experiments, water vapor and CO_2 flux were monitored with Li-COR 6262 analyzers. Light intensity (W m^{-2}) (Li-COR LI190SA), and temperature (°C) were measured just above the plant canopy. Soil temperature was measured at multiple locations in each pot using thermocouples (OME-GA, Type T). All sensors were hardwired to Campbell data loggers and data collected and averaged on 5-min intervals. Flow of air into each EcoCELL was monitored with a Sierra Instruments mass flow meter, and at night a known amount of CO_2 was permeated into the incoming air to allow for calibration of flows. Mercury concentration in irrigation water monitored over the course of both experiments was 2.0–3.6 ng l^{-1}. For detailed descriptions of experimental designs see Griffin et al. (1996), Gustin et al. (2004), and Obrist et al. (2004).

Statistical comparisons, t-tests and ANOVAs, ANCOVAs, and regression analysis were done using STATVIEW (SAS Institute, Inc.), and MINITAB for Windows 13.32. Area-under-the-curve integrations were done using SIGMA PLOT. Significance was considered when $p < 0.05$.

Results and discussion

Tub experiment results

It has been shown that in general, mercury flux from soil follows a diel pattern following solar intensity, with emissions lowest at night and increasing with first light to peak at midday and then declining to a nighttime low (Figures 1 and 2) (cf. Engle et al. 2001; Coolbaugh et al. 2002; Gustin et al. 2003). Mercury emissions from soils are strongly correlated with incident light increasing and decreasing as light intensity changes (Coolbaugh et al. 2002; Gustin et al. 2002). Figure 1 shows Hg emissions measured from unenriched substrate at a SWC of 4 and 15%. Emissions at 15% were significantly greater than those measured at 4% and exhibit a clear diel pattern. Emissions from dry soil were fairly constant and exhibited a slightly greater flux during midday and deposition at night. Figure 3 shows the mean and standard deviation of midday (1100–1300 h) Hg fluxes, measured from the same substrate used to generate the data in Figure 1, during days with full sun before and after the addition of water to achieve 23% SWC. Fluxes were measured from one tub in the end of May (top panel) and the other the beginning of June (bottom panel). In both experiments, water was added to achieve 23% soil moisture late in the afternoon on day 2 shown in Figure 3. Although not shown in Figure 3, immediately after water addition, there was no observed subsequent increase in emissions as has been reported for the addition of moisture to dry desert soils (cf. Lindberg et al. 1999; Nacht and Gustin 2004).

In May (top panel of Figure 3), the unenriched soil dried more slowly than in June (bottom panel) as shown by the decline in SWC. Mercury flux from the
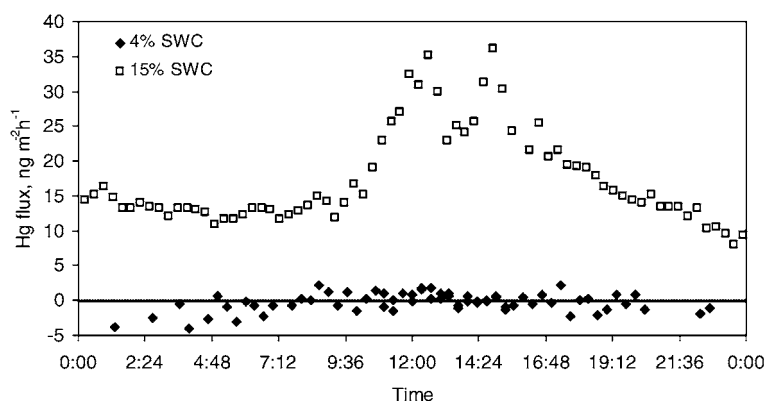
Figure 1. Diel Hg flux from unenriched soil at a SWC of 4 and 15%. Note that all fluxes from the soils wetted to 15% SWC are significantly elevated relative to that from the soil with 4% SWC.
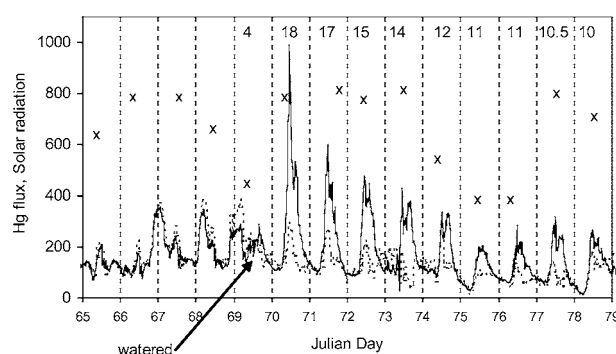

Figure 2. Mercury flux (ng m^{-2} h^{-1}) measured simultaneously from two tubs of Hg-enriched soils. Only one tub (solid line) was watered to obtain a 23% SWC. SWC (%) is shown at the top of the graph and 'X' is maximum midday solar radiation (W m^{-2}).

tub that dried more slowly was totally suppressed the day after watering and only after SWC became $\sim$20% (3 days after watering) were emissions significantly enhanced above that occurring from the dry soil (Figure 3). For the tub that dried more rapidly, the day after watering SWC was 15% and Hg flux was significantly enhanced above that measured from dry soils and similar to that occurring from the slow drying tub at a similar SWC. Midday Hg emissions at a SWC of 15% were approximately five times greater than that occurring from the original dry soil. Using the data from both of these experiments at a SWC $\leq$ 20%, a good correlation between SWC and midday Hg flux was obtained:

$$\text{Log midday Hg flux, ng m}^{-2}\text{h}^{-1} = 0.045(\pm SD = 0.002)$$
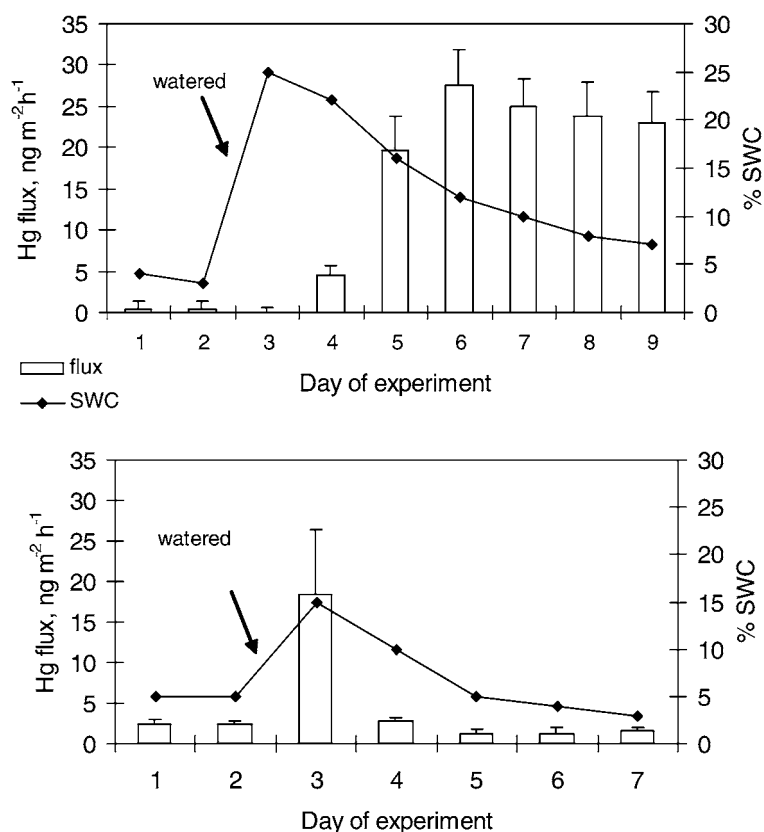$$* \text{SWC}, \% + 0.2(\pm 0.04),$$
$$(r^2 = 0.97, p < 0.0001).$$

Figure 3. Mean midday and standard deviation (1100–1300 h) of Hg flux measured from unenriched soil as function of soil wetting to 23% and subsequent drying (bars). SWC is shown as line. Top panel contains data collected at the end of May 2003 and the soil dried slowly. The lower panel has data collected at the beginning of June 2003 and the soil dried much more quickly.

In an experiment with two tubs of Hg-enriched soils (3 μg g^{-1}), two Tekran 2357 A instruments and switching units linked to flux chambers were used to monitor Hg flux simultaneously (Figure 2). For the first 5 days fluxes were measured from dry substrate to ensure that emissions from the two tubs were comparable. During this period, nighttime fluxes in some cases were significantly higher ($\sim$400 ng m^{-2} h^{-1}) than the daytime peak emissions (200 ng m^{-2} h^{-1}), deviating from the typical diel pattern. Elevated nighttime Hg emissions have been suggested to be due to the interaction of atmospheric oxidants with the soil surface (Zhang and Lindberg 1999; Engle et al. 2004). Elevated ozone concentrations were reported during these evenings (40 to 50 ppb as compared to $<$ 20 ppb on other evenings and most days) at air quality monitoring stations in the Reno area. Nighttime peaks in ambient air ozone concentrations in the Reno area are thought be due to transport of

air masses from California into the Reno area (A. Gertler, Desert Research Institute, personal communication). It is thought that the measured nighttime increases in Hg emissions may be due to ozone interaction with the soil. Engle et al. (2004), in the same greenhouse as used for these soil moisture experiments, exposed a variety of soil types to ozone in the dark at constant temperature and found that in the presence of ozone, Hg^o release from soils was increased by 40–95%. They also did experiments using ambient air and ozone concentrations in the chamber were similar to outside air. They also measured elevated ozone concentrations in the greenhouse. This indicates that during the experiments for this project ozone in ambient air could have been entering the chamber. Engle et al. (2004) hypothesized that the enhanced emission of Hg was due to ozone out competing Hg^o for binding sites on the soil surface, a mechanism similar to that which has been proposed for water.

After 5 days, the Hg-enriched soil in one tub was watered to attain a soil moisture content of 23%. With initial watering on Julian day 69.5 fluxes did not significantly increase nor were they suppressed. However, on the day after watering, midday fluxes in the wet tub were significantly elevated above that measured from the dry soils by 5 times and then gradually declined with time as the soils dried. Mercury emissions from the wet soil, over most of the day, were greater than that measured from the dry soil, however fluxes were similar at night. On Julian Days 75 and 76 daytime emissions in the wet and dry tubs were reduced as light was reduced due to cloud cover. There was a good correlation between midday Hg flux measured on sunny days and soil moisture content:

$$\text{Log midday Hg flux,ng m}^{-2}\text{h}^{-1} = 0.041(\pm 0.006) * \text{SWC}, \% + 2.0(\pm 0.1),$$
$$(r^2 = 0.89, p = 0.008).$$

Note that the slope for this equation for Hg enriched soil is similar to that derived for the relationship for the logarithm of flux vs. SWC for unenriched soils. The different intercepts are due to the different soil Hg concentrations.

Nighttime fluxes from the wet and dry soils on days 73 and 74 were elevated and variable. During these nights ozone concentrations were again elevated in the Reno area (>40 ppb). Measured Hg emissions from the dry soil were higher than the wet substrate during this time.

To investigate whether long-term maintenance of SWC resulted in continued elevated flux over time, the same soils as those used in the experiments described above were maintained at 13% SWC for $\sim$50 days and then increased to 23% for 14 days. Flux was monitored from dry soils in all tubs prior to wetting and compared to ensure that they were not statistically significantly different for wet–dry tub pairs. Wet–dry tub pairs, consisted of two with enriched Hg soil, one with unenriched soil, and another with unenriched soil amended with $HgCl_2$ to obtain a concentration of 0.1 $\mu g\ g^{-1}$ (Figure 4). As has been shown, midday mean Hg flux (1100–1300 h) from dry soils during sunny days was significantly greater than emissions measured in the dark (000–300 h) for all three soil types (Figure 4).
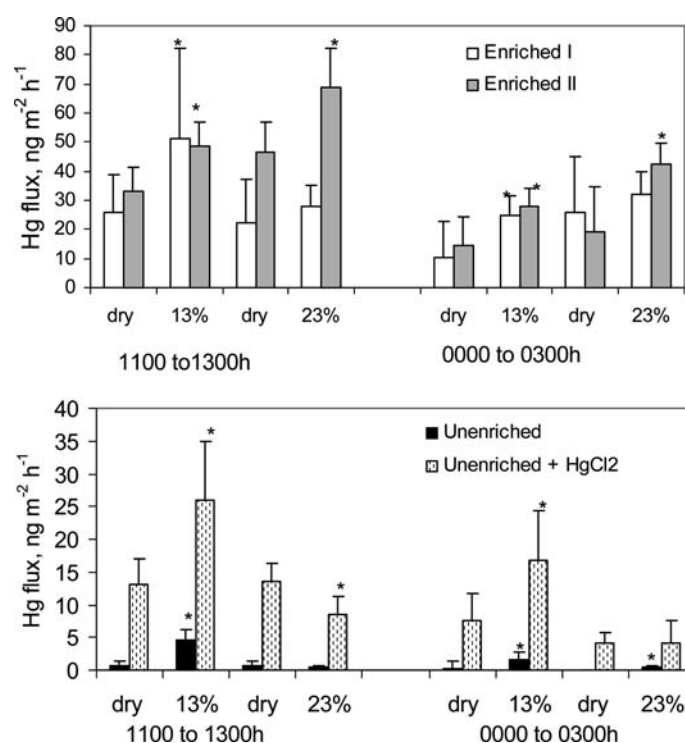
Figure 4. Mean and standard deviation of midday (1100–1300 h) and nighttime (0000–0300 h) flux from dry soils, and soils maintained at 13 and 23% SWC for 50 and 14 days, respectively. Data averaged is only that for days with full sun. ANOVA analysis was done to determine if fluxes were statistically significantly different between wet and dry tub pairs of each of the four exposure types: two tub pairs of Hg-enriched soil (3 $\mu g\ g^{-1}$), one tub pair of unenriched soil (0.02 $\mu g\ g^{-1}$) and one tub pair of unenriched soil plus $HgCl_2$ (0.1 $\mu g\ g^{-1}$). Asterisks indicate when fluxes from the wet tubs were significantly different than dry tub replicate ($p < 0.05$).

With the addition of water and maintenance of 13% SWC, midday and nighttime mean Hg fluxes from enriched soils remained elevated by ∼2 times above that measured from the dry soils for entire 50 day experiment (Figure 4). Asterisks in Figure 4 indicate that Hg fluxes measured from the wet tubs, were statistically significantly different from that of the paired dry tub. At 13% SWC, wet soil emissions were significantly greater than dry soils at midday and night. For the unenriched soil, at 13% SWC Hg fluxes were ∼4 times greater than that from dry soils, and for the $HgCl_2$ amended soil they were ∼2 times greater. Upon increasing the SWC to 23%, Hg emissions from the unenriched soils were suppressed, and for only one wet soil of an enriched pair were emissions statistically significant enhanced above that for the dry substrate. The enriched substrate had a higher water holding capacity than the Oklahoma soils so it is possible that the soil pores were not saturated enough to totally inhibit emissions.

Addition of water to dry desert soils in amounts less than needed to saturate the soil surface has been shown to cause an immediate enhancement of Hg emissions (Lindberg et al. 1999; Zhang et al. 2002; Nacht and Gustin 2004). These experiments showed that depending on soil water holding capacity, an initial suppression of flux could occur if sufficient water was added. Once the SWC became less than saturated, diel Hg flux would be significantly enhanced above that measured from dry soils especially during the day.

A similar enhancement of pesticide flux has been reported to occur after precipitation events and due to elevated SWC. Bardsley et al. (1968) observed an immediate release of pesticide with soil wetting and suggested that the addition of water facilitated desorption of Trifluran from soils due to competition between the herbicide and water for binding sites. Parmele et al. (1972) and Harper et al. (1976) reported that a diel pattern in volatile loss of 2-4 D and Trifluran occurred only from moist soils. They found that maximum releases from moist soils were observed during midday when high surface heating would enhance volatilization and atmospheric turbulence promoting movement of the pesticides from the soil surface. A similar response to wetting was observed for unenriched soils in Figure 1. Spencer and Cliath (1973) proposed that the observed diel pattern in release of pesticides from soils, whose surface concentrations of the pesticide had been depleted, was influenced by water movement in the soil facilitating transport of pesticide within the soil column to the soil–air interface. This process was described as the 'wick effect', whereby capillary action causes water and pesticides to move towards the soil surface as the soil dries and water evaporates. Simultaneously with water movement other chemicals are transported as mass flow. These substances can be left at the soil surface as the water evaporates. Surface processes then facilitate and enhance their release to the air.

In a similar manner, Hg could be transported with water as both Hg^o and Hg(II) towards the soil–air interface, and both could be left at the soil surface as the water evaporated. Some Hg^o could be volatilized with the water. Surface process that would facilitate release and volatilization of Hg left at the soil–air interface include photoreduction of Hg(II) and desorption of Hg^o with incident light (Carpi and Lindberg 1997; Zhang et al. 2001; Gustin et al. 2002), increases in temperature (Lindberg et al. 1979), precipitation events (Lindberg et al. 1999) and atmospheric turbulence (Poissant et al. 1999). This 'wick effect' would explain why soil drying rate would influence the amount of Hg emitted. When soil dries rapidly the surface Hg pool would be recharged for only a short amount of time by the 'wick effect', whereas the slow drying of soils would result in a longer period of recharge of Hg at the soil surface.

Mesocosm experiments

In the mesocosm experiment with Hg contaminated soils, watering in the early evening (~1800 h) caused a pulse of Hg to be released daily over the duration

of the experiment ($\sim$1.5 years). Prior to tree planting, watering times were altered (Figure 5) and in all cases the Hg flux response, measured at the EcoCELL level, was immediate and large (an increase of $\sim$3500 ng m^{-2} h^{-1}), and gradually declined to previous rates over $\sim$3 h. When watering occurred close to daybreak, the increase in flux associated with the increasing light was not as dramatic as usual because emissions were already elevated due to watering. Although the magnitude of the EcoCELL flux after watering was greater than the observed midday peak, the amounts of Hg released with the watering event and during daylight hours (obtained by calculating the area under the curve) were similar ($\sim$13 μg).

Flux chambers placed directly on the soil recorded the response to watering at the same time as the EcoCELLs, however, the measured response was not as great (increase of 500 ng m^{-2} h^{-1}) (Figure 4). In addition, midday Hg fluxes measured using the dynamic flux chambers (500–1200 ng m^{-2} h^{-1}) were not as great as those measured at the whole cell level (2000 ng m^{-2} h^{-1}). The dampening effect on the diel pattern that was observed at the EcoCELL level when the watering was done close to sunrise was also observed with the flux chamber. The lesser flux response to watering measured by the flux chambers is perhaps due to the fact that the watering was by drip irrigation and the chambers were placed in between irrigation lines from which water migrated laterally underneath the chamber. Because of their location, flux chamber emissions would increase as the water permeated the soil under the chamber, whereas the whole cell flux was influenced immediately by the watering.

The significant difference between the measured flux chamber and EcoCELL fluxes suggests that there is some discrepancy between the flux measurement methods. During an international Hg flux method measurement workshop in 1997, flux chambers were shown to underestimate emissions with respect to micrometeorological methods (cf. Gustin et al. 1999; Wallschlager et al. 1999). It was hypothesized that this was due to low chamber turn over rates, which were all greater than a minute. Two subsequent papers demonstrated that especially for enriched soils a higher turnover rate was necessary due to suppression of emission potential at lower flow rates (Lindberg et al. 2002; Zhang et al. 2002). In earlier work, Gao et al. (1997) suggested that if the air passing through a dynamic flux chamber did not simulate adequately turbulent atmospheric flow conditions, the flux of gases across the soil–air interface could be underestimated. Other factors that could influence the chamber flux is the location of the inlet air concentration measurement, and/or suppression of processes controlling Hg flux due to physical placement of the chamber on the surface, and/or reduction in incident light on the soil exposed in the flux chamber.

Mercury flux is calculated using the difference in air concentrations for the inlet and the outlet of a gas exchange chamber, divided by the surface area exposed, times the flow through the chamber. To calculate whole EcoCELL flux, Hg concentrations were measured in the inlet air ducts after air filters, and at the center of the EcoCELLs at 1 m height. In contrast, the chamber inlet
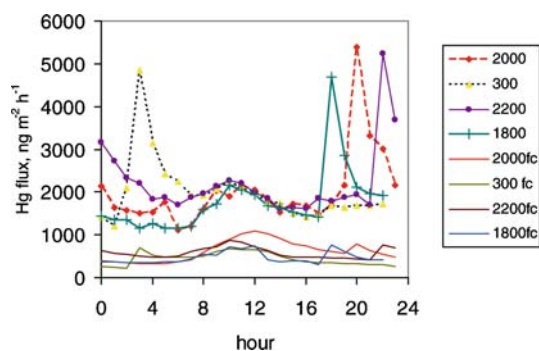
Figure 5. Response of EcoCELLs and field chamber (fc) fluxes to watering at different times of the day. Data was collected in April 2001 prior to planting and is only for days with full sun. The numbers in the legend denote the time of watering.

and outlet air Hg concentrations were measured directly above the Hg emitting soil surface. Thus, the inlet air for the EcoCELLs was clean outside air, whereas the inlet air for the flux chamber was contaminated air within the
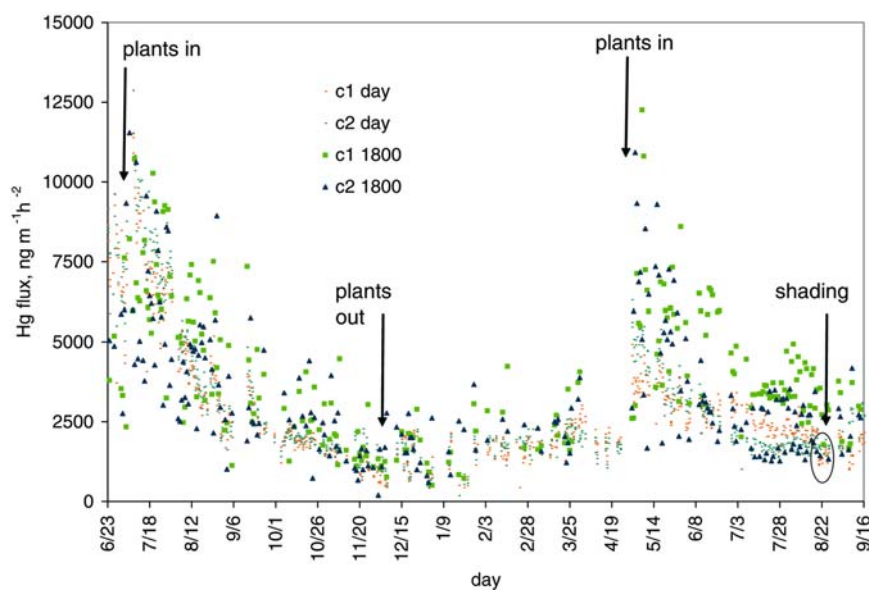

Figure 6. Mercury flux measured at midday (1100–1300 h) and at time of watering (1800 h) for EcoCELL 1 (c1), which was planted in the first year (7/5/00–11/16/00), and EcoCELL 2 (c2), which was planted both years (7/5/00–12/6/00 and 4/25/01 to 9/3/01), during the experiment with Hg-enriched soils (12.3 μg g^{-1}). Note that EcoCELL 1 was disturbed as though being planted 4/25/01. Data shown is only for sunny days. Data labeled shading is that collected when a shade cloth was suspended from the ceiling in the unplanted EcoCELL.

mesocosm. Since the air masses being used to calculate the concentration gradient for the two methods were different, this may be one factor causing the calculated flux difference.

One turnover of air in the EcoCELLs occurred every 6 min whereas for the dynamic flux chamber the time was $\sim$20 s. It seems unlikely that the flux chamber was suppressing the flux given the high flushing rate of the chamber. Additionally, the same wavelengths of visible light and UV light passing through the EcoCELLs walls and ceiling passed through the flux chamber, with the intensity of light in the visible realm beneath the chamber slightly reduced by 15% and ultraviolet by 5% (measured with an Ocean Optics Spectral Radiometer; see Gustin et al. 2002).

Flux measured with the chamber was however, significantly higher than that predicted for dry soils of similar Hg concentrations using a linear regression equation developed from flux chamber data collected *in situ* during sunny days (110 ng m^{-2} h^{-1}; cf. Zehner and Gustin 2002). This suggests that elevated SWC (20%) of the EcoCELL soils could be promoting an elevated flux.

Over the course of the EcoCELL experiment with contaminated soils, the peak flux response to watering at 1800 h varied, mimicking the general trends in midday fluxes (from 1100 to 1300 h) and was of similar magnitude to the peak midday flux (Figure 6). Each time the soil was disturbed for planting, the effect of watering on Hg flux was exacerbated as were midday emissions. In the first year, the peak Hg flux due to watering and at midday declined as the trees leafed out. Before the trees were removed in late November and early December 2000, the flux response to water addition was at its lowest. After removal of the trees, the peak flux response to watering and the midday peak gradually increased as light intensity on the soil increased (cf. Gustin et al. 2004). In April of the second year, only one EcoCELL (c2 in Figure 6) was planted. The peak response to watering was usually greater than the average midday peak for both EcoCELLs. As the leaves developed the peak response to watering in the planted cell overlapped with the midday peak. The flux response to watering was significantly greater in the unplanted cell relative to that in the planted cell after the leaf area index became > 0.5 (Figure 5). The greater flux response to watering in the unplanted cell may be due to a greater availability of Hg^{o}. More photoreduction of Hg(II) to Hg^{o} could occur in the exposed soil than the soil in the planted cell where incident light was reduced by $\sim$40%.

After development of a plant canopy, the amount of water released to the air in the unplanted cell with each irrigation event was approximately 2 times that released in the planted cell. Using the data for August and assuming solubility of Hg^{o} in water of 60 μg l^{-1} at 20 °C, the amount of Hg^{o} that could potentially be dissolved in the water and emitted as a function of evaporation in the unplanted cell was 0.2 μg. The amount of Hg released based on calculation of EcoCELL flux with watering was 13 μg. Significantly more Hg was released than could have been dissolved in the water. This suggests that desorption of

Hg from the soil surface and perhaps displacement of Hg^o in soil gas with the addition of water are important processes whereby Hg is released from soil with water addition.

As water moves into the soil column, it may displace Hg^o adhered to the soil. Johnson et al. (2003) investigated Hg and CO_2 in soil gas using two types of gas wells in this mesocosm experiment. They found that Hg^o concentrations measured in soil gas at midday from soils at 8–9% SWC were significantly lower (5000 μg l^{-1}) than that measured after increasing SWC to 18–24% (15000 μg l^{-1}). Additionally, Gustin et al. (2004) found that as the volume of water added to the EcoCELL soil was increased, whole cell Hg fluxes increased. These two observations indicate that increases in SWC could be important for desorbing Hg^o from soil particles and moving it into soil–air space.

Towards the end of this experiment, soils in the unplanted cell were shaded with a cloth that was hung near the ceiling. Incident light on the soil surface was reduced by 25–44%, similar to the reduction of light on the soil due to a full leaf canopy (15–42%, $n = 26$). Prior to shading, Hg fluxes that occurred after watering in the unplanted cell were significantly greater than those measured in the planted cell (difference of 1280 $\pm$ 150 ng m^{-2} h^{-1}) (Figure 6). With shading the difference in the flux response to watering between the two EcoCELLS was no longer significantly different. This is indicated in Figure 6 however, it is not easily seen given that the shading experiment lasted 6 days while the data shown reflects 1.5 years. Mercury fluxes at midday after watering, measured by the flux chambers in the unplanted mesocosm when shaded, were significantly less ($p < 0.05$) than those measured prior to shading. Once again these observations indicate that incident light is an important process that works in concert with SWC promoting Hg emissions from soils.

Watering in the large mesocosm experiments that utilized intact monoliths of tall grass prairie produced different results. This experiment differed from the first experiment in that irrigation occurred from the ceiling, the soil had very low Hg concentrations, and there was little exposed soil. Because of the high amount of vegetation cover, the soil surface did not dry regularly on a daily basis and remained moist. No consistent flux response to watering was evident at the ecosystem level for watering done in the morning at ~11 am or at night. Data were compared in several ways. T-tests were done comparing EcoCELL fluxes measured 1 h before and after watering for the daytime and nighttime, for winter, spring and fall, separately, and over all seasons. Out of 32 comparisons, 6 were statistically significant for the day and 5 for the night. Additionally, because of the diel variation in Hg emissions, ANCOVA analyses were done using diel time as a covariate. The latter is appropriate for light and temperature vary as function of time and strongly influenced the flux (Figure 7). There were no statistically significant differences between the fluxes measured on the day before and day of the rain event ($p = 0.116$) and the day of the rain and the day after the rain event ($p = 0.98$) for data in Figure 7. Similarly there were no statistically significant differences between chamber
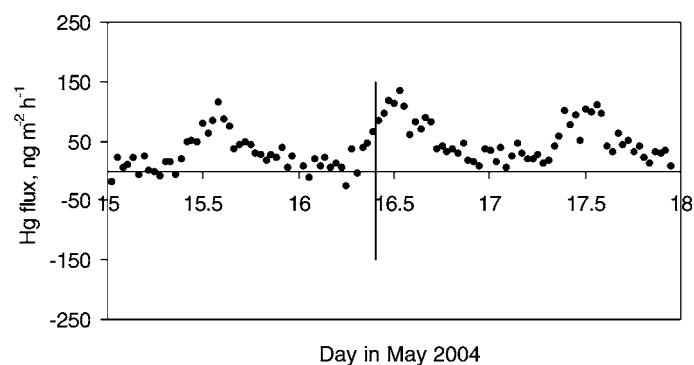
Figure 7. Mercury flux measured from one EcoCELL containing tall grass prairie vegetation before and after watering in May 2004. Watering denoted by straight vertical line.

measured fluxes pre- and post-watering. The chamber experimental design may have limited the potential for this method to measure a change in flux with watering, for it was not removed during watering and water would have to migrate from the surrounding soil to beneath the chamber.

Similar to the contaminated soil mesocosm experiment, EcoCELL midday fluxes measured from the unenriched soils in June (20–30 ng m^{-2} h^{-1}) were greater than those measured with the chamber placed on the soil surface (3.4 ± 4.5 ng m^{-2} h^{-1}). Fluxes measured from the same dry soils in the long-term soil moisture tub experiments described above were 0.7 ± 0.6 ng m^{-2} h^{-1} and from moist soils (13% SWC) were 4.7 ± 1.6 ng m^{-2} h^{-1}. It is hypothesized that because the tall grass prairie soil was heavily vegetated and shaded in this experiment, and the soil surfaces remained fairly moist, the pulse of Hg emissions immediately after watering observed in the contaminated soil mesocosm experiment was not observed. However, the elevated SWC is most likely responsible for the high Hg fluxes measured from the wet soils in the EcoCELLs relative to those measured from the same soil when dry.

Conclusion and conceptual model

Based on the data described above, the following conceptual model is proposed for the observed influence of precipitation and SWC on Hg flux. With a precipitation event Hg° will be released from a dry soil to the air due to desorption from the surface as the more polar water molecule replaces Hg°. As water penetrates the soil, additional Hg° will be desorbed from the soil and move into the soil air space. Elemental Hg in soil gas will be displaced towards the surface as the water moves down in the soil column. If Hg(II) is present in the soil some may dissolve in soil water. As the soil dries and water is evaporated, Hg(II) and Hg° will be transported towards the soil surface as mass flow concurrent with water movement. A component of this Hg is then subsequently deposited at the

soil–air interface as the water evaporates. Elemental Hg^o left at the soil surface could then be released by processes facilitating desorption. Hg(II) adsorbed onto soil particles could be photoreduced (cf. Carpi and Lindberg 1997; Zhang et al. 2001; Gustin et al. 2002) and then released as Hg^o. Release would be highest in the middle of the day with maximum sunlight and turbulence, facilitating photoreduction and vertical movement of gases away from the soil surface. Photoreduction of Hg(II) at the soil surface could also produce a pool of Hg^o available for release by other processes. Light clearly enhances the release of Hg from moist soils, with a greater flux from moist soils observed during bright sunny days than cloudy days; and an enhanced diel pattern of emissions from wet soils as compared to dry soils. In contrast, ozone or atmospheric oxidants are more efficient at releasing Hg from dry rather than moist soils.

This process of mass movement of Hg, promoted by water evaporation, from within the soil column towards the soil surface could be an important mechanism whereby soil surfaces would be constantly recharged in Hg derived from deeper in the soil. At the soil–air interface Hg^o and Hg(II) would remain adsorbed to the soil surface until soil wetting, incident light, increased temperature, increased relatively humidity and/or the presence of atmospheric oxidants would promote the release of Hg^o to the air.

Acknowledgements

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